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Final Report

## ENCAPSULATED AEROSOLS

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U.S. ARMY CHEMICAL CORPS RESEARCH AND DEVELOPMENT COMMAND  
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## Final Report

### ENCAPSULATED AEROSOLS

#### I Summary

The three general approaches to aerosol encapsulation\* studies during this investigation are liquid phase encapsulation, condensation, and coagulation.

Liquid phase microencapsulation (a technique which has been utilized with considerable success in a number of applications) was shown to be practical in some encapsulation systems which could be dispersed in aerosol form. Dibutyl phosphite was encapsulated by polyvinyl formal and polyethylene.

The condensation method produced several encapsulated aerosols in good yield. Various material combinations exhibited a wide variation in stability and other physical properties. Three examples of encapsulated aerosols which were produced in good yield by the condensation method are lauric acid on dioctyl phthalate, lauric acid on tricresyl phosphate, and ammonium chloride on tricresyl phosphate.

Examples of a nonwetting combination, ammonium chloride and clay, and of an inverting combination, ammonium chloride and phosphoric acid, were encountered in systems in which all encapsulation requirements except correct surface properties seemed to be met.

Modified condensation methods, in which vapor phase monomers were polymerized and condensed on the core particles, or in which the monomer was condensed on the core particle and then polymerized, were developed. The polymerization reaction of conjugated polyolefins involving nitrogen

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\*The term aerosol, as used in this report, refers to the entire system of dispersed material and gas. However, in order to simplify the discussion, when such expressions as "encapsulated aerosols," "liquid aerosols," etc., are used, it is implied that the adjective refers to the dispersed phase.

dioxide was used in developing these modifications.

Coagulation in a representative system during settling was investigated. After an hour's coagulation a fairly large fraction of heterocoagulation was observed.

Three types of microcapsules--solid on liquid, solid on solid, and liquid on solid--were investigated using inertial forces and electrostatic forces to enhance heterocoagulation. The investigations of coagulation of solid on liquid and solid on solid involved formation of a solid polymer from a solution by vaporization of the solvent. Thus, at the time of capsule formation, the aerosol pairs actually were liquid on liquid and liquid on solid. Under conditions of aerosol coagulation none of the systems investigated produced a coherent polymer film.

Some encapsulation of glass microspheres with liquid films was accomplished by high velocity mixing of two aerosol streams in a Venturi throat. Passing the two aerosol streams through electrostatic charging units of opposite polarity caused a high degree of cross coagulation when the streams were brought together, and resulted in an excellent yield of liquid on glass microcapsules.

## II Introduction

While a considerable amount of research and development effort has gone into specific approaches and methods for microencapsulation by a number of organizations in the past decade, this study is the first in which a general investigation of the basic principles involved in aerosol encapsulation has been attempted. New techniques were developed and evaluated by laboratory tests, and the effect of pertinent physical and chemical parameters on the encapsulation process was investigated. The particle size range of interest was from one micron to one hundred microns. Coated aerosol particles of all combinations of liquids and solids were studied.

## III Discussion of Methods of Approach

There are a number of approaches to the preparation of encapsulated

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aerosols. No one method of coating aerosols is suitable for all particle sizes and materials. Each method has its area of applicability and while there is some overlap, these areas are necessarily limited by the physical and chemical properties of the materials involved.

One approach to aerosol encapsulation is the indirect method of forming the capsules while suspended in liquid solution, followed by spray evaporation of the solvent. The feasibility of this method has been proved in several commercial applications, but this approach is cumbersome and is restricted to a narrow range of conditions.

A similar method, even less adaptable, is that of coacervation. The addition of various materials to sols often produces a precipitate of droplets (coacervates) stabilized at the interface by a film. This film can be used in some systems to encapsulate the droplets. This is followed by isolation and spraying.

A potentially versatile approach to aerosol encapsulation is by condensation of a supersaturated vapor on the aerosol particles. In this method the aerosol containing the particles to be coated is mixed with another gas stream rich in the vapor of the encapsulating material. As this mixture is allowed to cool, the aerosol particles serve as condensation nuclei for the vapor. This method is limited because the coating material must be volatilized without decomposing. Furthermore, the aerosol material must not appreciably volatilize or decompose at the temperature used to vaporize the coating material. Also certain properties of both materials, such as their polar or nonpolar character, are critical and influence the ability of the aerosol particle to act as a condensation nucleus.

The process of coagulation can be utilized to encapsulate aerosol particles after dispersion. Ideally this involves the agglomeration of small particles around a larger particle of a different species.

In simple coagulation due to the Brownian movement of the particles, the coagulation coefficient between particles of different size is greater than that between particles of the same size. This is discussed by Fuks,<sup>1</sup>

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1. Fuks, N.A. The Mechanics of Aerosols. Translated from the Russian as CWL Special Publication 4-12, p 338.

who gives a table of numerical values. But we may expect in a real system to have a large number of small encapsulating particles coating a single central particle. In such a system, the rate of self-coagulation of the small particles will be greater than the heterocoagulation rate because of the relative numbers involved. This point is illustrated in Table I. A coating 0.5  $\mu$  thick on a 10  $\mu$  diameter sphere requires a volume 0.34 that of the central sphere. The table shows the number of small particles of various sizes required to produce this coating (assuming that the particles coalesce and spread over the central particle to form a uniform coating), the coagulation coefficients between particles of these sizes, and the ratio of rate of self-coagulation between the coating particles and the rate of heterocoagulation.

Table I  
PARTICLE SIZE EFFECTS ON COAGULATION EFFICIENCY

$d_2$ (Diameter of Encapsulating Particles)	Number of Particles of Diameter $d_2$ Needed to Form a 0.5 $\mu$ Coating Over a 10 $\mu$ Particle	$k_{1-2}$ (Coagulation Constant Between a 10 $\mu$ Particle and a Particle of Diameter $d_2$ )	Ratio of Coagulation Rate Between Particles of Diameter $d_2$ to Coagulation Rate Between Particles of Diameter $d_2$ and 10 $\mu$
0.1 $\mu$	340,000	$220 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$	$10^4$
1	340	$10.3 \times 10^{-10}$	$10^2$
10	0.34	$3.0 \times 10^{-10}$	1

The above figures show that, as the encapsulating particles are made smaller, the number of them which are needed increases much more rapidly than does the coagulation coefficient between particles of the two sizes. As a consequence, the small particles will coagulate with each other more rapidly than with the large particles. Thus there is no advantage in

making the encapsulating particles relatively very small, since they will rapidly self-coagulate to bring their particle size to one approaching the core aerosol.

The coagulation coefficient between the two types of particles can be increased by imparting an acceleration to one particle relative to the other. This principle is employed in commercial devices such as the Jet Pulverizer<sup>2</sup> or the Micronizer.<sup>3</sup> In these devices the particles collide with each other in a rapidly moving air stream, which results in a grinding of the particles. According to the manufacturers, a coating action may also be achieved.

A somewhat similar principle is described in a series of patents by Marshall.<sup>4</sup> In Marshall's devices the particles to be coated, in aerosol or fluidized bed form, are subjected to a spray of the encapsulating material. This material may be either a solidifiable liquid or a solution from which the solvent is removed in a subsequent drying step. Provision is made for building up the coating by recycling the coating particles.

These impact methods are better for coating large particles and are probably not suitable for particles smaller than 10  $\mu$  in diameter. Electrostatic forces may also be used to enhance heterocoagulation. Aerosol particles will accumulate substantial electrical charges upon passing them through corona discharges.<sup>5</sup> Normally a fraction of the particles in any aerosol has acquired a charge with about half of this fraction positively charged and half negatively charged. Passage of an aerosol through a corona discharge will tend to charge all of the particles with the same charge. This can be done quite efficiently if optimum conditions are realized.

- 
2. Manufactured by the Jet Pulverizer Co., Rt. 73, Palmyra, New Jersey.
  3. Manufactured by Sturtevant Mill Co., Harrison Square, Boston, Mass.
  4. Marshall, D. E. U.S. Patents 2,561,392; 2,561,393; 2,561,394; 2,561,395; and 2,579,944.
  5. Dawkins, G. S. Electrostatic Effects in the Deposition of Aerosols on Cylindrical Shapes. TR No. 15, Engineering Experimental Station, University of Illinois, March 15 (1958).

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Another possible approach to aerosol encapsulation is through heterogeneous chemical reaction between components in the aerosol particles and components in the gas phase.

It may be necessary or advantageous to combine two or more of the above basic approaches in order to encapsulate particles of a particular material with a film of another particular material. Of the four possible phase combinations of encapsulated aerosols--liquid on liquid, liquid on solid, solid on liquid, and solid on solid--the general problems encountered are more difficult with the liquid core microcapsules than with the solid cores. The four types listed in order of increasing difficulty to prepare are liquid on solid, solid on solid, solid on liquid, and finally liquid on liquid. Examples of all four types were prepared during the course of this work.

#### IV Condensation Method

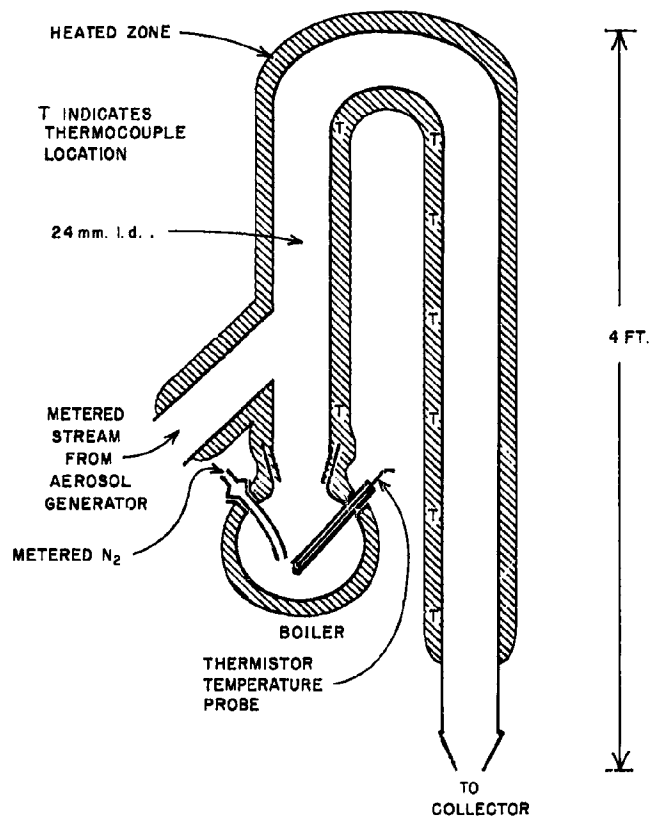
##### A. Apparatus and Procedures

The apparatus which was first used to prepare encapsulated aerosols by the condensation technique is shown in Fig. 1. Two metered streams of nitrogen, one carrying aerosol and the other carrying saturated encapsulating vapor, were mixed in the hot chimney as shown. The mixed stream was maintained at a temperature slightly above that of the boiler until it had traversed the "U" curve in the chimney and had started downward. Then the temperature was gradually reduced until it approached room temperature at the end of the heated zone. The temperature and temperature gradient were controllable by three individually regulated heating tapes wrapped around the chimney.

Aerosol was generated by means of a DeVilbiss nebulizer which discharged into a 20-liter bottle. Aerosol was dispensed from this bottle into the encapsulating apparatus by means of a metered nitrogen stream.

The aerosol was collected in one of two ways, on a Millipore filter or passed into a small settling chamber and allowed to deposit on a glass slide. Examination was made by means of the phase contrast microscope.

Early attempts to observe encapsulation by including a fluorescent dye (Rhodamine) in the aerosol to be encapsulated were unsuccessful. It



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FIG. 1  
CONDENSATION APPARATUS FOR ENCAPSULATED  
AEROSOL PREPARATION

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was not possible to see the dye, either visually or by fluorescence, in individual particles observed through the microscope. Attempts to observe bulk quantities of aerosol in a fluorescent photometer, using a reflection technique, were not successful because of the high background and low level of emission from the sample.

## B. Encapsulation Pairs Examined

### 1. Benzoic Acid Coating on Dibutyl Phthalate

The condensation apparatus was first tried using dibutyl phthalate aerosol mixed with benzoic acid vapor. The aerosol consisted of particles of about 2  $\mu$  diameter, and upon the basis of later experiments the particle concentration was estimated to be of the order of  $10^5$  particles per cc. The benzoic acid vaporizer was maintained at a temperature of 134°C, at which the vapor pressure of the acid is 10 mm. The best results were obtained with an aerosol flow rate of 1 liter/min mixed with vapor at a flow rate of 40 cc/min.

Under these conditions opaque round particles of 10-15  $\mu$  in diameter were formed; they resembled neither the transparent droplets of liquid aerosol nor the needle-like particles obtained from benzoic acid alone under these conditions. Thus it seems fairly certain that the round particles were dibutyl phthalate drops encapsulated in benzoic acid.

An experiment under similar conditions, but with a twofold increase in aerosol flow and a fourfold increase in aerosol flow, yielded a mixture of unencapsulated liquid droplets and benzoic acid needles. This suggests that the residence time in the latter case (about 15 sec in the cooling zone) was not long enough to permit condensation of the vapor on the aerosol.

The encapsulated aerosol, when collected on a dark background Millipore filter, was visible as a white powder. After standing several hours the white color disappeared. Presumably the dibutyl phthalate either dissolved or soaked through the benzoic acid coating.

### 2. Lauric Acid Coating on Dioctyl Phthalate

Dioctyl phthalate was used in this experiment instead of dibutyl



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phthalate, because of its lower volatility. Lauric acid proved to be more satisfactory than benzoic acid. It solidifies in a compact form instead of tending to be fluffy; also, its solubility in either butyl or octyl phthalate is less than that of benzoic acid.

Diethyl phthalate aerosol having particles of about  $1\ \mu$  diameter, when treated with lauric acid vapor, formed particles of  $6-9\ \mu$  in diameter that were distinctly different in appearance from either pure octyl phthalate aerosol or lauric acid condensed in the absence of aerosol. The untreated lauric acid particles were about  $14\ \mu$  in diameter. Similar experimental conditions were used later in the ammonium chloride-butyl phthalate system. The boiler was operated at two temperature levels in a number of runs.

In this series the weight ratio of lauric acid to diethyl phthalate varied between 0.36 and 45. The optimum ratio was between 2 and 5. Figure 2 is a photomicrograph of this encapsulated aerosol. The capsules average about 14 microns in diameter.

A qualitative evaluation of the effect of the coat-core weight ratio on yield and stability is presented in Table II for this pair and for lauric acid-tricresyl phosphate.

### 3. Lauric Acid on Tricresyl Phosphate

When tricresyl phosphate was substituted for diethyl phthalate this combination produced stable capsules in good yield at very low coat-core weight ratios.

### 4. Ammonium Chloride on Dibutyl Phthalate

The coating of dibutyl phthalate with ammonium chloride was investigated somewhat in detail. The aerosol, after passage through the heated system, contained spherical transparent particles between  $3$  and  $9\ \mu$  in diameter. The density of the aerosol, integrated over the 20 minute duration of an experiment, was found to be  $2.6 \times 10^{-4}$  g/liter. The sample of encapsulated material was collected only during the second 10 minutes of this period.

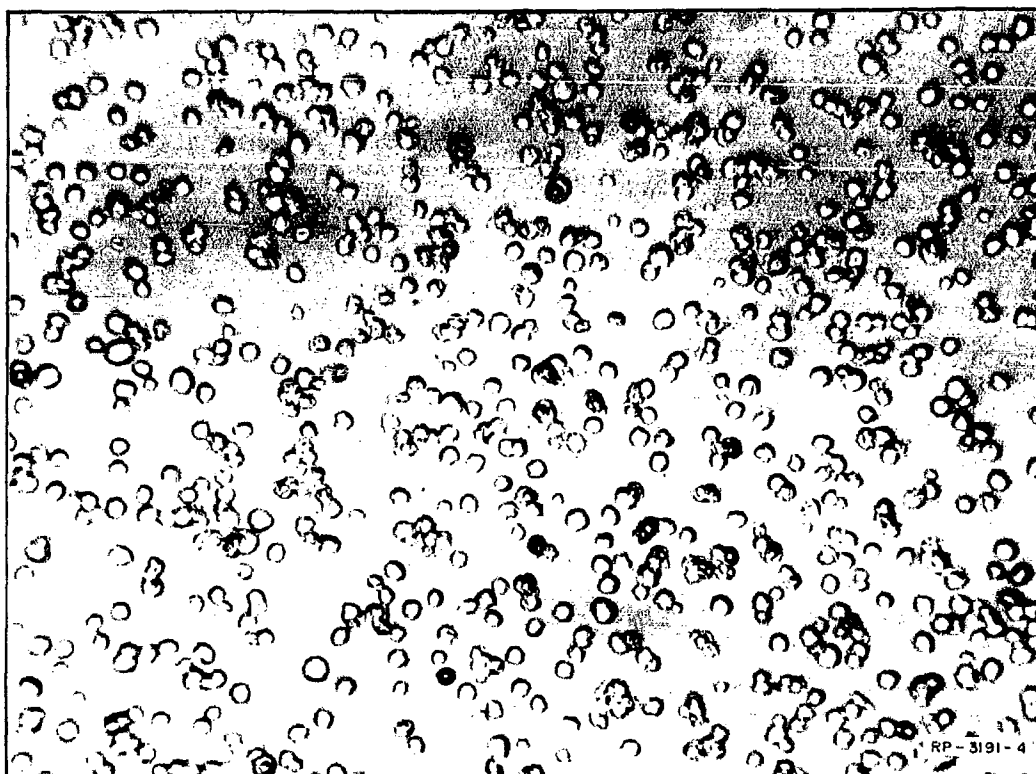


FIG. 2  
DIOCTYL PHTHALATE DROPLETS ENCAPSULATED IN LAURIC ACID  
Magnification 230X

Table II

## COATING THICKNESS AS A FUNCTION OF CAPSULE STABILITY

Nitrogen Flow Rate (ml/min)	Wt Ratio (coat/core)	Results
Lauric Acid on Dioctyl Phthalate		
1050	0.4	Some capsules formed; crushed upon touching
1100	0.7	Slightly better yield; some strength improvement
1200	1.4	Improvement in yield and stability; irregular shapes noted
1300	2.2	Good yield of 11-13 $\mu$ stable capsules
1030	4.5	Good yield of 14 $\mu$ stable capsules
1300	45	Thickly coated capsules plus excess lauric acid particles
Lauric Acid on Tricresyl Phosphate		
1025	0.3	Irregular capsules easily broken
1050	0.6	More stable capsules
1100	1.2	Stable capsules

Four different operating conditions were used, with results which were not greatly different. In all cases the number of particles collected was not great, much fewer than with an unencapsulated aerosol. The predominant type of particle in all these experiments was semi-opaque when viewed with transmitted light and glistened brilliantly when illuminated obliquely from the side. These particles were distinctly different in appearance from either unencapsulated aerosol particles, which were quite transparent, or from ammonium chloride particles, which were irregularly shaped and opaque. The capsules were found in a variety of sizes, ranging from about 6  $\mu$  up to 50  $\mu$ . Most of the particles were below 15  $\mu$  in diameter.

Figure 3 is a photomicrograph of the product from a typical encapsulation experiment. Two prominent features are an irregularly shaped ammonium chloride particle and one of the largest capsules observed, about 50  $\mu$  in diameter.

Other encapsulated particles may be seen in the background. These are difficult to identify from the photograph since they could not be brought into focus simultaneously with the large particles, but visually they were identified as capsules. The medium-sized capsules are about 15-20  $\mu$  and the small ones are about 6  $\mu$  in diameter. An unencapsulated droplet may be seen about one-half inch from the large capsule.

The operating conditions used were as follows. Initially, 300 cc/min of nitrogen was passed through ammonium chloride maintained at 210°C (the vapor pressure of ammonium chloride at this temperature is 10 mm) and mixed with an aerosol stream of 1000 cc/min; a few encapsulated particles were formed. This corresponds to a weight ratio of  $\text{NH}_4\text{Cl}$  to butyl phthalate of 34. Next, the ammonium chloride-butyl phthalate ratio was increased to 89, primarily by reducing the aerosol flow rate. In addition to spherical particles of the kind observed before, irregularly shaped particles were obtained which are presumably ammonium chloride particles.

##### 5. Ammonium Chloride on Tricresyl Phosphate

It was found that higher gas flow rates through the condensation chamber favored capsule formation. At lower flow rates, as in the ammonium



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FIG. 3  
PRODUCT OBTAINED BY CONDENSING AMMONIUM  
CHLORIDE VAPOR ON DIBUTYLPHthalate AEROSOL  
Magnification Approx. 230X

chloride-dibutyl phthalate system, a large excess of ammonium chloride was needed for capsule formation. A large part of this excess was deposited on the walls. This effect can be explained if the dimensions and geometry of the condensation apparatus and the gas stream velocities are considered carefully. The calculated Reynold's numbers are small throughout the system at all flow rates used.

Following the merger of the vapor-laden nitrogen stream with the aerosol nitrogen stream, the flow, even at the highest flows used, was laminar. The condensation tube has an internal diameter of 4 cm; thus it would have been necessary to have used flows in excess of 70 liters per minute to depart from the laminar flow regime. At the low total flow rates (about one liter per minute) there was little or no mixing of the two nitrogen streams as they entered the superheater section of the 4-cm-diameter tube. They passed through the condensation tube more or less as two discrete streams, flowing side by side, and the small amount of encapsulation observed at low flow rates was probably due to diffusional transport of the ammonium chloride vapor out of one stream into the other. A large fraction of the ammonium chloride was, however, transported to the tube wall. As the total flow was increased, more and more mixing occurred in the region where the two streams flowed into the common tube. These better-mixed streams allowed larger fractions of the ammonium chloride vapor to be transported by diffusion to the aerosol droplets in the condensation tube.

At a total flow rate of 11 liters per minute, a large yield of stable 3  $\mu$  capsules was produced at a coat-core weight ratio of 5.4.

#### 6. Ammonium Chloride on China Clay

A pure china clay (Putnam Clay) aerosol was next used in an effort to encapsulate a solid with a solid. No encapsulation of the clay particles by condensing ammonium chloride was observed over a wide range of weight ratios. This appeared to be a case of nonadhesion between the clay and ammonium chloride surfaces.

#### 7. Ammonium Chloride on Phosphoric Acid

Phosphoric acid was selected as an interesting candidate for

comparison with the less polar phosphate and phthalate ester liquids which had been encapsulated with ammonium chloride. This condensation system behaved in a surprising manner: By some mechanism, either penetration of the liquid droplets by the condensing ammonium chloride, or by self-nucleation followed by heterocoagulation, or a combination of these, the system inverted, and phosphoric acid-coated ammonium chloride crystals were produced. Figure 4 is a photomicrograph showing the liquid coating on the solid cores.

C. Wettability of Components in the Ammonium Chloride Condensation Systems

The effect of condensing ammonium chloride on drops of dibutyl phthalate, tricresyl phosphate, and phosphoric acid suspended on glass rods was observed. The ammonium chloride encapsulated the dibutyl phthalate and the TCP, but no film formed on the phosphoric acid surface.

V Condensation Polymerization Method

Of the possible materials for use in coating aerosol particles, those which will form a continuous film over the particle surface are obviously the most interesting from the point of view of application. Solid or very viscous film forming materials are generally polymeric in nature; thus, all of the approaches to polymer microencapsulation are important. Encapsulation of microparticles by polymer films can be accomplished in the liquid phase by techniques which will be discussed in Section VII. Polymer encapsulation of microparticles simultaneously with dispersion as aerosols, or after dispersion, has proven to be extremely difficult. Centrifugal and fluid bed devices for polymer encapsulation have successfully produced capsules of sizes ranging down to about 300  $\mu$  in diameter,<sup>6,7</sup> but

- 
6. Southwest Research Institute has designed and fabricated a device which utilizes centrifugal force to form capsules.
  7. Wurster, Dale of Univ. of Minn. School of Mines has developed a fluidized bed spray coating apparatus.

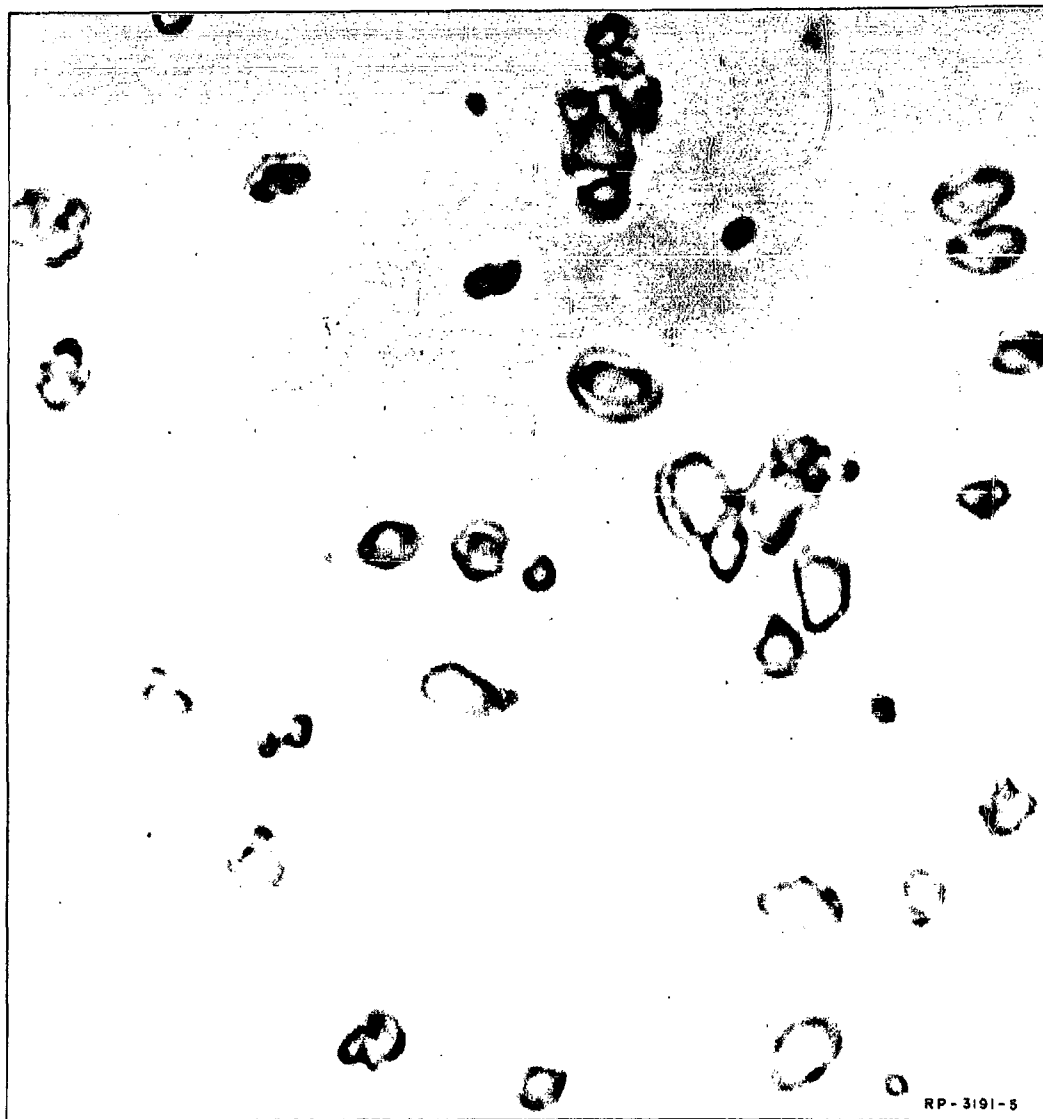


FIG. 4  
AMMONIUM CHLORIDE CRYSTALS ENCAPSULATED IN LIQUID PHOSPHORIC ACID  
Magnification approx. 2000x



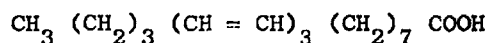
these devices are not practical as yet for producing capsules in the micron size range. Also, the development of methods for the production of polymers in aerosol systems has not been particularly successful to date. Polymer reactions usually require many minutes to hours to produce significant yields and the catalytic systems are very sensitive to traces of catalyst poisons.

There are, however, a few vapor phase and heterophase polymerization reactions which are relatively fast. Examples of these reactions were selected for study to determine the feasibility of this approach.

Both types selected involved the polymerization of a conjugated diolefin in the presence of and by reacting with gaseous nitrogen dioxide at low concentration.

In the vapor phase, diolefins will react with nitrogen dioxide to form a polymer, a kind of nitro-gum.<sup>8</sup> This reaction is very rapid and is relatively insensitive to external effects. The polymer produced is tough and elastic, and a good film former; however, it is inherently unstable and the capsules formed have a finite lifetime.

The material selected for use as the encapsulating liquid monomer in the heterophase reaction system was tung oil. Eighty percent of tung oil is eleostearic acid, which is an 18 carbon unsaturated fatty acid with three conjugated double bonds, i.e.,



A. Vapor Phase Diolefin Monomer Plus Nitrogen Dioxide to Produce Polymer Coated Aerosols

The encapsulation of phosphoric acid by the isoprene-nitrogen dioxide polymer was attempted. Phosphoric acid aerosol from a De Vilbiss nebulizer was added to the bottom of a reaction vessel in a nitrogen carrier at 6 liters N<sub>2</sub>/min. At this aerosol flow rate the concentration of phosphoric acid was 0.32 mg/liter. Some of the later runs were made at 7 liters N<sub>2</sub>/min, and 0.60 mg/liter of phosphoric acid.

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8. Leonet, G. Chimie & Industrie, 57, 351 (1947).

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Isoprene, (2 methyl butadiene 1,3) vapor was added into the same line with the phosphoric acid droplets. Nitrogen was passed at the rate of 3 ml/min through liquid isoprene in a bubbler thermostated at 0°C in an ice slush bath. The effluent from the bubbler was 3 ml nitrogen plus 1 ml isoprene. This represented 0.2 ml/liter or 0.5 mg/liter of isoprene in the reaction mixtures.

Nitrogen dioxide was introduced through a separate line into the bottom of the reactor. The nitrogen dioxide was also metered by bubbling a known rate (3 ml/min) of nitrogen through liquid nitrogen dioxide thermostated at 0°C in an ice slush bath. By this procedure 0.3 ml/liter (0.5 mg/liter) of nitrogen dioxide was added to the system in the reaction vessel. The isoprene and the nitrogen dioxide formed the polymer gum which condensed on the phosphoric acid droplets. This is a condensation which is induced by chemical change rather than a physical change; however, the actual condensation process appears to be the same as the physical phase change condensation process.

Samples of the aerosol material were collected by gravity settling on Teflon sheets for a 20-minute period. The material was washed from the Teflon into beakers with 10 ml of distilled water and titrated with one tenth normal sodium hydroxide solution.

The acid available in the samples from the encapsulating runs was compared with the acid available on blank (nonencapsulating) runs. The fraction encapsulated was considered to be the ratio of the amount of unavailable acid to the amount of acid in the blank run, the amount of unavailable acid being the difference between the blank and the encapsulating runs. Table III shows the results of the encapsulation runs performed using isoprene, tung oil, or butadiene monomer plus nitrogen dioxide.

Titration were also made using 10 ml of acetone first to dissolve the capsules, then 10 ml water. With this technique encapsulation runs and blank runs showed the same amount of acid.

In one isoprene polymer encapsulation run, the water resistance of the polymer capsules was investigated. Starting with a 31% encapsulation the capsules were stored in distilled water at room temperature for 5-1/2

Table III  
POLYMER GUM ENCAPSULATION IN THE AEROSOL PHASE

Flow Rate liters N <sub>2</sub> /min	Concentration of Components in Aerosol mg./liter						Reaction Time (min)	Percent Encapsulation (comparative titration)
	Phosphoric Acid (liquid dioplets)	Polyolefin Vapor			Nitrogen Dioxide Vapor			
		Butadiene	Isoprene	Tung Oil	Nitrogen Dioxide Vapor			
7.0	0.60	0.5	-	-	-	1.3	1.0	25
6.0	0.32	-	0.2	-	-	0.5	0.5	16
6.0	0.32	-	0.2	-	-	0.5	0.5	50
7.0	0.60	-	0.2	-	-	1.3	0.4	71
6.0	0.32	-	0.2	-	-	0.5	0.5	75
7.0	0.60	-	0.2	-	-	1.3	0.4	77
7.0	0.60	-	0.7	-	-	0.4	0.4	92
7.0	0.60	-	-	-	cnk*	1.3	0.4	35
9.0	0.47	-	-	-	2.2	1.0	2.3	35
7.0	0.60	-	-	-	cnk*	1.3	0.4	38
7.0	0.60	-	-	-	cnk*	1.3	0.4	41
11.0	0.38	-	-	-	3.6	0.8	2.0	43
11.0	0.38	-	-	-	3.6	0.8	2.0	44
7.0	0.60	-	-	-	cnk*	6.5	0.4	57
7.0	0.60	-	-	-	cnk*	6.5	0.4	63
7.0	0.48	-	-	-	0.12	1.3	3.0	30**

\*\*Used 4:1 phosphoric acid-tung oil emulsion in nebulizer.

\*cnk (concentration not known). In these experiments the 7 liters/min of aerosol were passed over the tung oil which was at 165°C.

hours. At the end of the period 9% of the phosphoric acid remained encapsulated.

Butadiene was substituted for isoprene in one encapsulation experiment. Nitrogen was bubbled through liquid butadiene at  $-80^{\circ}\text{C}$  in a dry ice-isopropyl alcohol bath. The behavior of the butadiene was similar to that of isoprene.

B. Liquid Phase Polyolefin Monomer Plus Nitrogen Dioxide to Produce Polymer Coated Aerosols

The apparatus was modified to use tung oil as the monomeric material. This system was made up of a complete condensation apparatus plus an aerosol polymerization apparatus. The condensation system was a modified La Mer aerosol generator in which the tung oil was vaporized and superheated. In some of the experiments the phosphoric acid aerosol was passed through the La Mer generator; in others nitrogen was used to carry the tung oil vapor and this stream was mixed with the aerosol containing the core material in a jacketed condensation tube. After encapsulation of the phosphoric acid with the tung oil, nitrogen dioxide gas was introduced and the mixture was passed into a reaction vessel.

Figures 5A and 5B show the capsules of phosphoric acid in liquid tung oil before reaction, and, after reaction, the capsules with the tung oil polymer coat. The results of the tung oil polymer encapsulation experiments are listed in Table III.

Dibutyl phosphite was also used as a core material in tung oil polymer encapsulation. An attempt was made to give the dibutyl phosphite core a strong color with a brilliant blue oil soluble dye. The dye was no help, for it was as easy to differentiate between the capsules and the bare cores (which had not been dyed) as it was to distinguish between the capsules and the cores which had been dyed. In both cases microscopic examination revealed a difference in the appearance of the unencapsulated and the encapsulated particles.

The evaporation rate of phosphoric acid encapsulated in the tung oil polymer was compared with the evaporation rate of uncoated phosphoric acid droplets by exposing samples of each in the laboratory for sixteen hours.

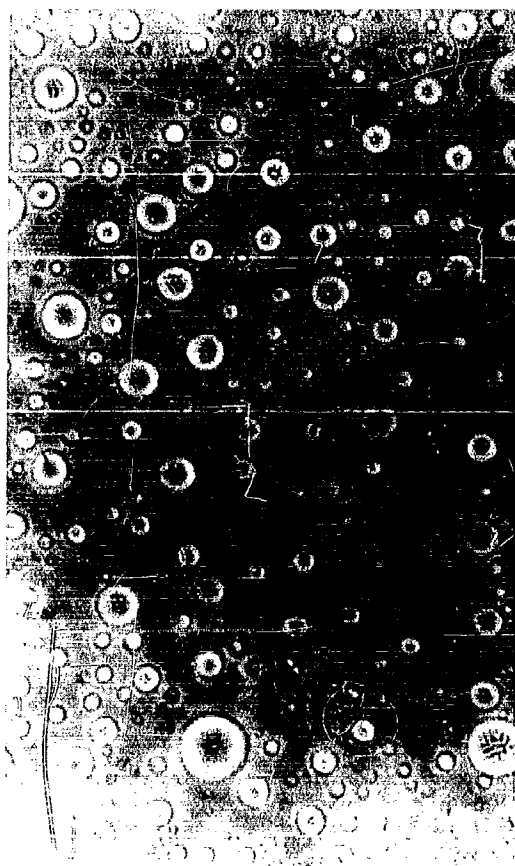


FIG. 5(a)

PHOSPHORIC ACID DROPLETS ENCAPSULATED  
IN LIQUID TUNG OIL  
Magnification 300x

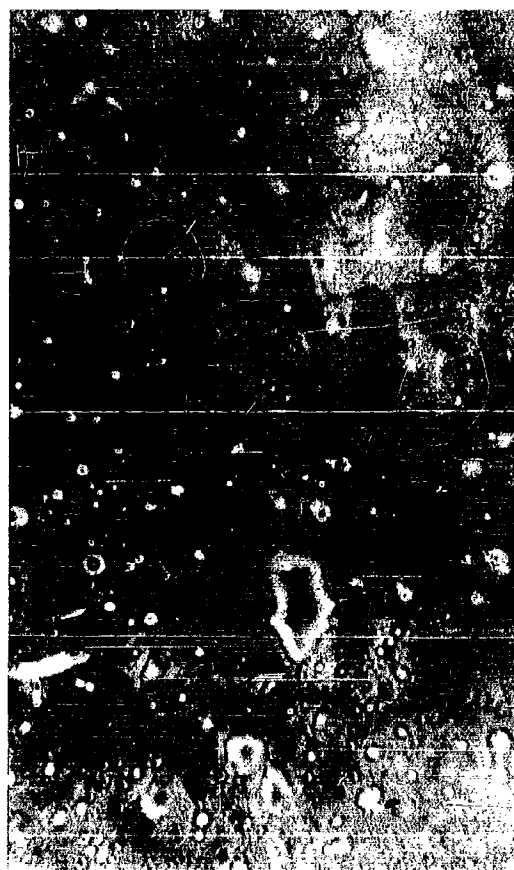


FIG. 5(b)

PHOSPHORIC ACID DROPLETS ENCAPSULATED  
IN TUNG OIL POLYMER  
Magnification 300x

RP-3191-II

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These samples were acetone treated and titrated as described in the last section. Forty-five percent of the uncoated acid evaporated and forty percent of the encapsulated acid evaporated.

Tung oil and phosphoric acid when mixed produce an unstable emulsion. They were used in a weight ratio of 4:1 phosphoric acid to tung oil in the De Vilbiss nebulizer to produce an aerosol. This aerosol was reacted with nitrogen dioxide. Thirty percent of the acid was encapsulated as determined by titration indicating that encapsulation occurred upon dispersion.

## VI Coagulation Method

### A. Coagulation During Settling

An apparatus was assembled to study encapsulation by coagulation; the main components of this system were the two aerosol generator units and the coagulation chamber. The core aerosol was generated with a glass spray nozzle, producing droplets of  $3\ \mu$  average size (number), with a fairly narrow size-distribution range. The coating aerosol was restricted to one of the long chain organic acids, and this aerosol was generated by vaporizing the organic acid in a nitrogen stream by use of a resistance heater. The organic acid underwent self-nucleation and passed into the coagulation chamber as supercooled droplets. The aerosol streams were mixed in the top of the coagulation chamber, which was a glass standpipe 100 cm long and 10 cm in diameter. The samples were collected on slides at the bottom.

The first aerosol pair studied was stearic acid on phosphoric acid. After 40 minutes of coagulation some heterocoagulation had occurred, but much more was noticed when the coagulation time was increased to 60 minutes. Figure 6 is a photomicrograph showing 5 to  $10\ \mu$  agglomerates, in which the phosphoric acid droplets appear to be completely covered with stearic acid crystals.

### B. Coagulation by Inertial and Electrostatic Forces

Coagulation of aerosol droplets on other aerosol particles or droplets (utilizing external forces) was considered next. All of the encapsulating liquid aerosols which were paired with liquid cores were solutions



FIG. 6  
LIQUID PHOSPHORIC ACID DROPLETS COVERED WITH STEARIC ACID  
Magnification 900x

of polymers. Other liquids were also used when the encapsulation of solid cores was attempted.

### 1. Use of Polymer Solutions

Polymer encapsulation was attempted by dispersing solutions of various polymeric materials to form aerosols; the solvent was not permitted to vaporize until after coagulation of the liquid droplet with the core droplet or particle. The droplets of solution were prevented from evaporating by saturating the nitrogen in the aerosol with the solvent vapor.

### 2. Production of Solid Aerosols

In addition to solid on liquid aerosols, we considered liquid on solid and solid on solid aerosols. Glass was selected as being a convenient, representative, inert, solid material for the aerosol particle cores. Various sizes of very small glass spheres are available from Minnesota Mining and Manufacturing Company. The particle size range of the powder used was 80 percent  $10\ \mu$  to  $60\ \mu$  in diameter. The size distribution was bimodal with peaks at 10 and 45 microns. For purposes of calculation the aerosol was considered to contain one  $45\ \mu$  diameter particle for every five  $10\ \mu$  diameter particles.

Because it was necessary to have some method of dispersing the glass spheres as an aerosol and maintaining a reasonably uniform mass flow rate, a solid aerosol generator was designed and incorporated into the encapsulation apparatus shown in Fig. 7. The generator is the glass vessel with the dome-shaped top section shown on the left. When in operation, a 6 liter/min nitrogen flow through the apparatus carries the glass spheres into the column, where they remain suspended in the form of a very dense aerosol. The top, with its greater cross section, provides a disengaging space. After dropping its particle load back into the column, the nitrogen passes out through the looped exit line. About three quarters of the way up the column, there is a 3 mm diameter bypass connecting the column directly to the exit line. A small fraction of the nitrogen flow--carrying its particle load with it--passes through this orifice into the exit tube.



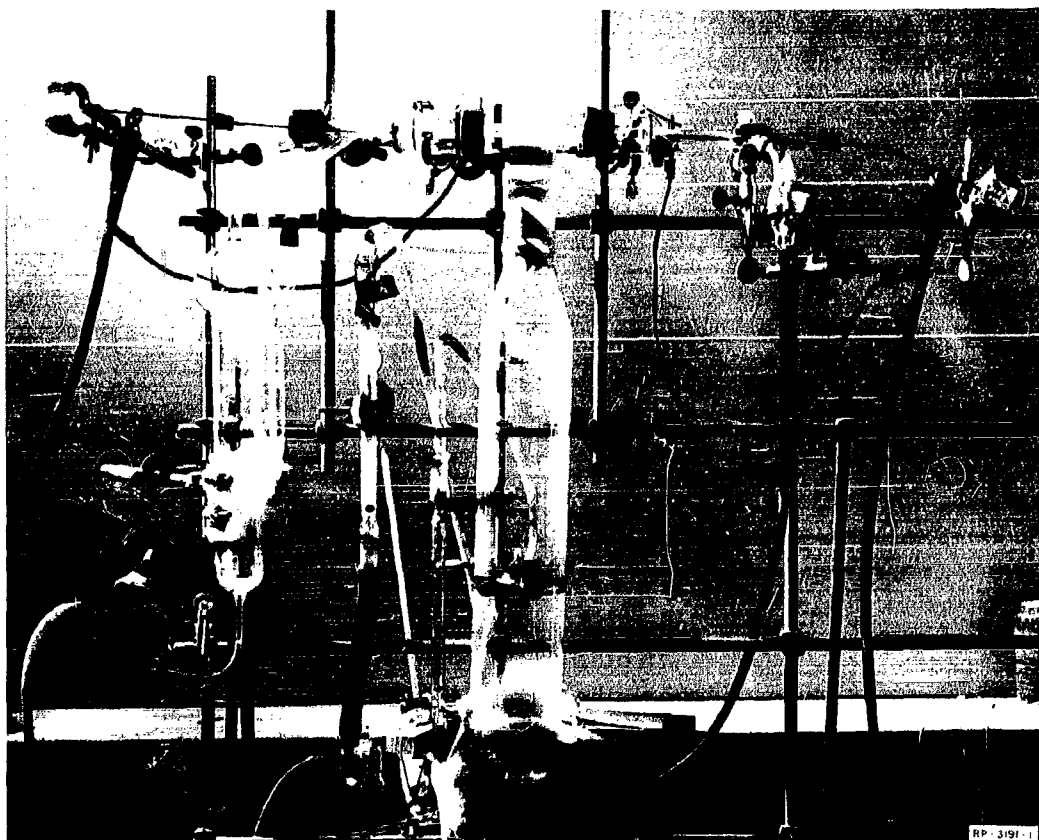


FIG. 7  
APPARATUS FOR ENCAPSULATION OF SOLID AEROSOL PARTICLES WITH LIQUID FILMS

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The ratio of the cross sectional area of the orifice to that of the exit line is critical and determines the depletion rate of the aerosol material.

Aerosol particle size, apparatus dimensions, nitrogen flow rate, and amount of aerosol material initially charged into the generator are all interrelated functions of successful generation of the solid aerosol.

The dimensions and conditions which produced a 1.5 mg/liter aerosol (100 particles/ml) for a period of more than 5 minutes are as follows:

Column length	25	cm
Column cross sectional area	65	cm <sup>2</sup>
Disengaging chamber cross sectional area	230	cm <sup>2</sup>
Exit line cross sectional area	1.6	cm <sup>2</sup>
Bypass cross sectional area	0.07	cm <sup>2</sup>
Nitrogen flow rate	6	liter/min
Wt of glass powder charge	0.5	gm

### 3. Venturi Mixer

Of the possible external forces which might be used to promote coagulation between two aerosols, electrical forces and inertial or mechanical forces appear to be the most promising.

Electrical charging experiments will be described later.

To investigate the change in encapsulation tendency caused by inertial forces, two simple devices were utilized. The first was a Venturi mixer, used to produce turbulence and thus to promote collisions between particles of different momentum. One liquid-liquid aerosol pair and three liquid-solid aerosol pairs were studied. The diameter of the ends of the Venturi was 11 mm; the throat diameter was 4 mm; and the side tube leading into the throat was 3 mm in diameter. The aerosol to be encapsulated was passed through the Venturi at gas flow rates from 7 to 20 liters/min. The encapsulating aerosol was introduced at a flow rate of 9 liters/min through the side tube into the Venturi throat. At the zone of impact the particles were exposed to moderately high-velocity collision conditions between species. At 20 liters/min the linear stream

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velocity was 24 meters/sec in the Venturi throat.

The first aerosol pair studied was diethylene glycol and commercial paraffin in n-hexane solution. In order to generate a commercial paraffin in n-hexane aerosol with a nebulizer, it was found necessary to dilute the solution to 0.25% commercial paraffin. The nitrogen carrying the paraffin solution was presaturated with n-hexane vapor.

After colliding in the Venturi throat, the mixed aerosol stream passed through a section which was heated to 80°C to insure rapid vaporization of the hexane solvent. Then the particles were collected, by gravity settling, on glass and Teflon slides for microscopic examination.

At first, the observations were misinterpreted, because the diethylene glycol droplets were quickly reduced in size by partial evaporation upon mixing of the diethylene glycol aerosol with the n-hexane commercial paraffin aerosol which contained no diethylene glycol vapor and produced an unsaturated condition in the mixture. After this condition was corrected, there was no evidence that encapsulation or heterocoagulation had occurred.

Subsequently, encapsulation of the 10-60  $\mu$  glass spheres with dibutyl phosphite and ortho phosphoric acid was attempted by means of mechanical impaction in the Venturi mixer. The flow rates were equal: 7 liters/min for the glass aerosol which was passed straight through the Venturi, and 7 liters/min for the dibutyl phosphite aerosol which was brought into the side tube. An intense yellow dye, Flurol 7GA from General Dyestuff Company, was added to the dibutyl phosphite.

Samples of the aerosol mixture were collected by gravity settling on glass slides for microscopic examination and compared in appearance with collected samples of the untreated glass spheres. The material collected from the Venturi mixer consisted of a mixture of glass spheres, which were faintly but definitely yellow in color, plus excess DBP in the form of 2-5  $\mu$  liquid droplets which were quite yellow.

Encapsulation was accomplished, but it was an inefficient encapsulation.

In the second liquid-solid pair experiment, phosphoric acid was the encapsulating material for the glass spheres. The extent of encapsulation was determined by the titration of the phosphoric acid found on a

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glass aerosol sample of known weight, size distribution, and total surface.

It was necessary to make blank phosphoric acid runs and subtract the results from those of the total acid. The mixed aerosol streams were introduced into the middle of the 10 cm diameter by 100 cm high aerosol chamber. A nitrogen flow of 9 liters/min was passed into the bottom. This provided a vertical gas velocity which carried the phosphoric acid droplets out through the top and allowed the larger glass particles to settle and be collected on 5.5 cm filter paper placed in the chamber at the 20 cm level.

The volumetric analysis showed that some encapsulation did occur. The over-all encapsulation efficiency, however, was only 2%. Of about 12 mg of phosphoric acid in the aerosol, 0.25 mg were in the film on the glass spheres. Assuming uniform distribution, the calculated film thickness was about  $0.07 \mu$ .

Microscopic observation of the material collected when a third liquid-solid pair of aerosols--dibutyl phosphite (dyed yellow) and talc--was passed through the Venturi mixer in the same manner revealed encapsulation to about the same degree as in the first two cases.

#### 4. Turbulent Mixing in Tube

We next considered the probability of encapsulation of one liquid droplet species with another by the action of turbulence in a long tube of high stream velocity.

A glass tube, 2 mm inside diameter by one meter long, was used. The two aerosol streams were admitted into the tube through a simple T. The tube was mounted vertically so as to exhaust into the upper half of the 10 cm x 100 cm aerosol chamber. Samples were collected by settling in the lower half of the chamber.

A polymer solution (3% polystyrene in methylene chloride) was used to produce the encapsulating material and phosphoric acid was again used as the core material. Both aerosol flow rates were 7 liters/min. The aerosol velocity in the tube was 75 meters/sec and the Reynolds number was about 15,000.

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Most of the aerosol material was deposited on the tube wall within a few centimeters of the point of entry. After building up to a steady state thickness, this material was re-entrained by the aerosol stream. The deposition and re-entrainment of the aerosol material had such an extreme effect on size distribution and composition of the ultimate effluent droplets that any interdroplet coagulation or encapsulation effects were completely masked.

#### 5. Electrostatic Particle Charging

The first aerosol charging cell designs were unsuccessful and a number of changes were made before a satisfactory design was achieved.

The charging cells were single-point corona discharge units, specially designed to minimize electrostatic precipitation while providing for efficient particle charging. The plates in these cells were shaped like flattened doughnuts with smooth, rounded inner surfaces of small longitudinal area. The aerosol stream passed around the needle point and through the center hole of the plate. The final design is shown in the units at the top of Fig. 7.

The ability of these charging cells to pass the charged aerosol particles was determined quantitatively by measuring the amounts of phosphoric acid collected from charged and uncharged runs. Thirty percent by weight of the charged phosphoric acid was passed. Also, the effect of charging on the particle size and particle-size distribution was investigated by microscopic observation. Figures 8A and 8B compare samples collected on Teflon slides of the charged and uncharged phosphoric acid aerosol.

The aerosol was charged by passing it through a positive corona discharge. As might be anticipated, the average droplet size is smaller after charging and the size distribution range is narrower, because the large droplets were precipitated in the charging cell.

Some of the same aerosol pairs which were investigated in the inertial force study were used again to determine the effect of electrostatic charging of aerosol particles on coagulation and encapsulation efficiency.

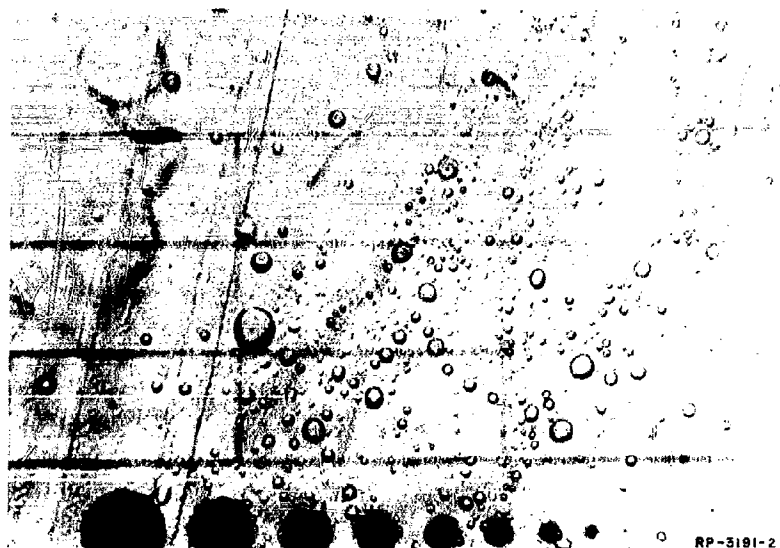


FIG. 8(a)

PHOSPHORIC ACID DROPLETS ON TEFLON  
Magnification approx. 400x

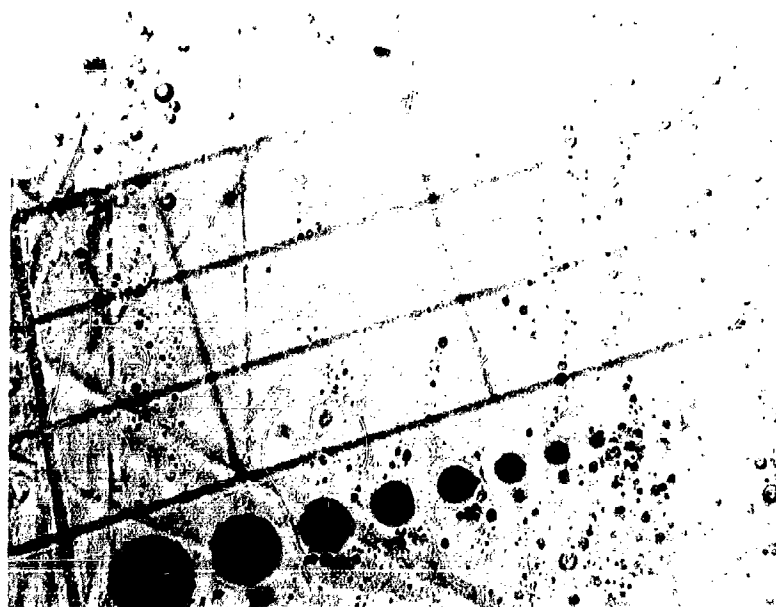


FIG. 8(b)

DROPLETS FROM IDENTICAL AEROSOL AFTER PASSING THROUGH  
POSITIVE CHARGING CELL  
Magnification approx. 400x

The first candidate pair was the 3% polystyrene solution in methylene chloride, and phosphoric acid.

The polymer solution aerosol was passed through a negative corona discharge at a rate of 7 liters/min. The maximum operating voltage allowed by the aerosol was 18 KV. (Higher voltage caused intermittent sparking.) At this voltage the current was 50  $\mu$ amps.

The phosphoric acid aerosol was passed through a positive corona discharge at a rate of 5 liters/min. This aerosol limited the maximum operating voltage to 9 KV with a current of 200  $\mu$ amps.

The apparatus was designed so that the two aerosol streams would come together head on, then change direction 90° and move out and down the aerosol chamber, as shown at the top, center of Fig. 7.

A section of the chamber was heated to vaporize the polymer solvent and the collector was situated below the heated section.

Microscopic examination of the material collected from this system revealed that the coagulation efficiency was greatly increased but that the capsules were inverted. The phosphoric acid encapsulated the polymer particles.

A second polymer solution-liquid core pair, cellulose nitrate in acetone and dibutyl phosphite, also failed to produce a polymer film microcapsule and also exhibited reverse encapsulation.

Next, the encapsulation of negatively charged glass spheres by positively charged phosphoric acid droplets was investigated. Figure 7 is a photograph of the apparatus set up for this system. The glass aerosol limited the operating voltage to 5 KV at a current of 1 milliamp. The glass aerosol flow rate was 7 liters/min.

Utilization of the encapsulating material appeared to be 100%. This is shown clearly in Figs. 9A and 9B. They are photomicrographs of the collected material from two experiments, identical except that there was no aerosol charging in 9A and the aerosols were oppositely charged in 9B.

The experiment which was performed to determine the effect of charging on the amount of aerosol material passed, in which positively charged phosphoric acid droplets were collected separately, rules out any

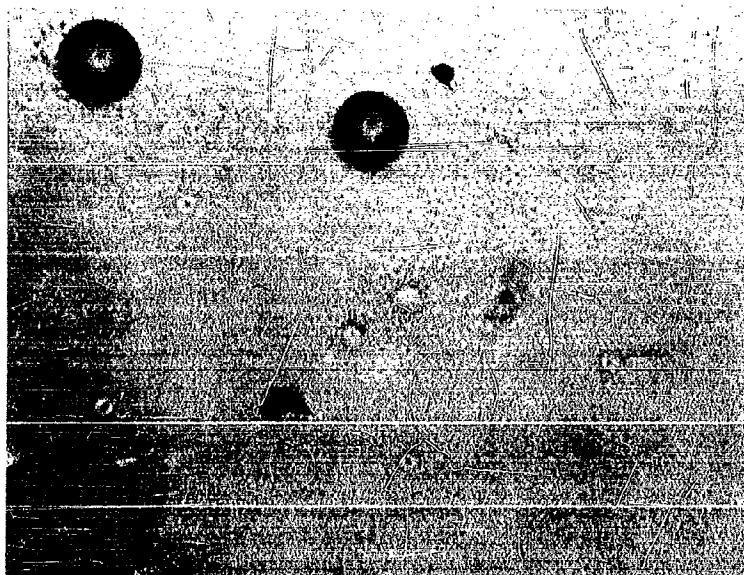


FIG. 9(a)  
GLASS SPHERES AND PHOSPHORIC ACID  
DROPLETS--NO AEROSOL CHARGING  
Magnification approx. 400x



FIG. 9(b)  
SAMPLE COLLECTED USING NEGATIVELY CHARGED  
SPHERES AND POSITIVELY CHARGED DROPLETS  
Magnification approx. 400x



repulsion effect between the collecting surface and the charged phosphoric acid droplets as the reason for the absence of acid droplets in Fig. 9B.

An aerosol was made of 3% polystyrene solution in methylene chloride. This aerosol was passed through the positive corona unit and used in an attempt to encapsulate negatively charged glass spheres. Again the heterocoagulation efficiency was excellent; however, the polymer did not form a film, but was present as isolated 2-5  $\mu$  particles adhering to the glass spheres even though the polymer was in the form of solution droplets at the mixing zone.

Vinyl chloride, an excellent film former, also failed to encapsulate the glass spheres when used under the same conditions in acetone solution.

## VII Liquid Phase Encapsulation

The encapsulation of water-sensitive materials with water-soluble or water-permeable polymers was studied. Dialkyl phosphites, dialkyl chlorophosphonates, and alkyl chlorophosphates were selected as models for water-sensitive substances. The encapsulating polymer must be selected according to the solubility and reactivity characteristics of the substance to be encapsulated. Consequently, it is not possible to select one polymer that can be used as an encapsulating agent for all of the above esters.

The reactivity of water-sensitive compounds can be adequately controlled by encapsulation. Depending on the water-solubility, water-permeability, or water-vapor transmission of the capsule wall material, the encapsulated compound will exhibit varying degrees of reactivity toward water.

As polyvinyl formal (Formvar) is permeable to water, the encapsulated substances in contact with water could be gradually extracted with water or could be allowed to react slowly with it.

The first experiments were carried out with dibutyl phosphite (DBP), using polyvinyl formal (Formvar, Shawinigan Resins) as encapsulating agent. Encapsulation was attempted by mixing dibutyl phosphite (1:1 weight ratio of DBP to Formvar) with a 5% solution of Formvar in a chloroform chlorobenzene mixture (1:4 weight, respectively). The resulting mixture was stirred

at room temperature, while petroleum ether (65-110°C), in an amount sufficient to cause incipient precipitation of the polymer, was dropped in slowly. Afterward, the mixture was cooled in an ice bath with gentle stirring for about a half-hour. The cooling produced precipitation of the polyvinyl formal onto the dibutyl phosphite droplets. The microcapsules formed were isolated by spraying the mixture with a De Vilbiss spray gun under a current of warm air. The particles were collected on a Mylar film and were scraped off as a dry powder from which an oil could be released by applying pressure. The size ranged from 2  $\mu$  to 10  $\mu$ . A higher ratio, 2:1, of phosphite to Formvar was also encapsulated as above. Higher ratios showed oil on the surface of the capsules, thus indicating that the phosphite was not completely encapsulated. By incorporating colloidal silica such as Santocel (Monsanto Chemical Company) or Cab-O-sil (Godfrey L. Cabot Company), higher ratios were encapsulated. The following weight ratios were used in two experiments carried out with colloidal silica: 1:4:25 for Santocel:Formvar:DBP, and 1/2:4.5:25 for Cab-O-sil:Formvar:DBP. The procedure was to add the silica to the dibutyl phosphite and to stir the mixture into the Formvar solution, which was then treated as above for precipitation of the polymer and isolation of the capsules. In both cases, a dry powder was obtained. The DBP could be released easily by applying pressure. Since the Formvar is permeable to water, the phosphite could be extracted by stirring the powder in water.

Attempts made to encapsulate isooctyl phosphite by the same procedure were not successful. This phosphite precipitated the resin and remained in the nonsolvent phase; consequently, upon spraying the mixture an oily powder was obtained.

Polyethylene (PE) was chosen as the encapsulating agent to be studied which would represent the hydrophobic polymers. The water-vapor transmission of PE varies with its molecular weight, steric configuration, and degree of crystallinity of its films. Dimethyl phosphite (DMP) was selected as a simulant for highly water-reactive compounds and was encapsulated in PE. A solution of a special proprietary formulation of PE was used as encapsulating agent. DMP was incorporated into the PE solution at a 1:1 ratio (PE to DMP). The microcapsules were isolated by spraying

the mixture into a stream of warm air which was directed to a Mylar surface, where the capsules were collected. These ranged in size from 2  $\mu$  to 12  $\mu$ . Figure 10 is a photomicrograph of PE capsules containing DMP. Although the capsules could not be wetted with water, it was possible to extract the phosphite gradually by vigorously stirring the capsules in water. About 25 minutes of vigorous stirring was required to detect any change in pH caused by dissolution of the phosphite in water. Faster release of the DMP was obtained by addition of a solvent for PE such as toluene or xylene. Capsules with negligible degree of water-permeability were obtained by substituting 25 percent of PE with paraffin. These capsules were not as hard as those made with PE alone, but were more stable to moisture.

Benzene phosphorus oxydichloride (BPOD), a highly reactive acid chloride, was encapsulated with PE using the same PE composition, but varying the ratio of PE to BPOD. Ratios of 1.5:1 (PE/BPOD) and higher were used because encapsulation was incomplete at the 1:1 ratio used for DMP. Fairly stable capsules containing from 30% to 40% BPOD were prepared. These could not be wetted with water, but the BPOD could be released gradually by stirring the capsules in water as described above for DMP. When capsules containing BPOD were exposed to air for a long period of time there was a gradual increase in weight due to slow reaction with water vapor and absorption of moisture.

Attempts made to encapsulate other compounds such as phosphoric acid, dibutyl chlorophosphate, and tributyl phosphate by a similar procedure were unsuccessful.

#### VIII Conclusions

A number of methods for liquid phase encapsulation of fine particles have been developed. Polymer materials, such as polyvinyl formal, or polyethylene may be used to encapsulate certain core materials by phase changes in liquid systems. The properties of the candidate core materials are critical in these systems and some core materials could not be encapsulated. This approach may be considered to be aerosol encapsulation;

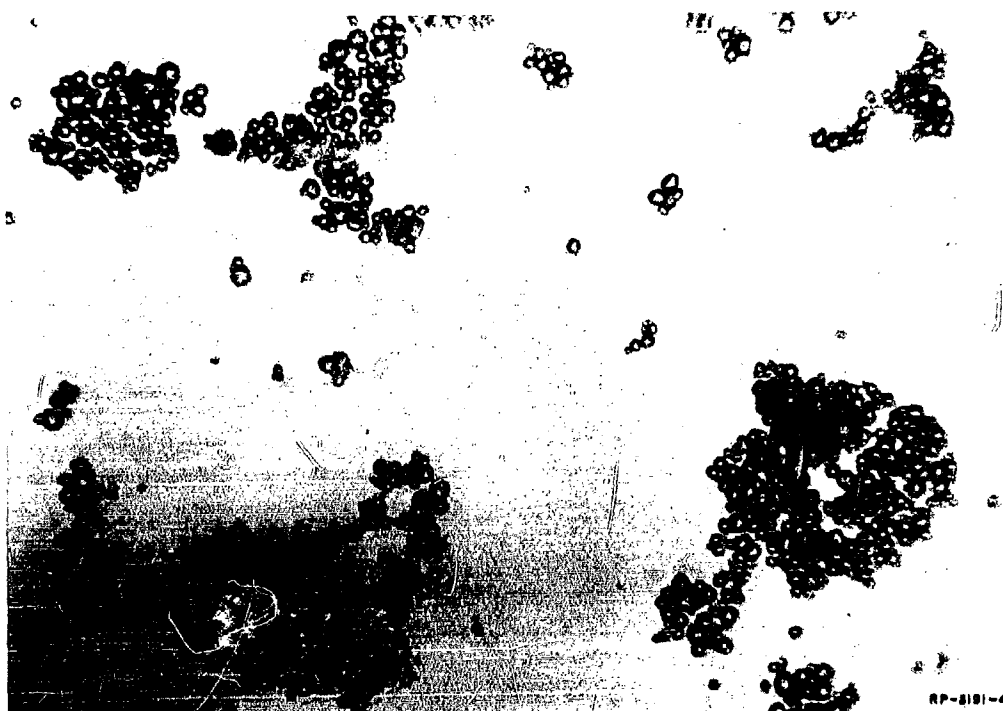


FIG. 10  
DIMETHYL PHOSPHITE DROPLETS ENCAPSULATED IN POLYETHYLENE  
Magnification approx. 400x

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however, it is via the route of microencapsulation in the liquid phase, followed by the treatments necessary to produce an aerosol from the capsules.

The condensation process is an excellent approach to aerosol encapsulation, if the combination of physical and chemical properties of the components in a system meet certain rather stringent requirements. The coating material must have an appreciable vapor pressure and the core material must be essentially nonvolatile at the process temperature; both materials must be chemically stable at the process temperature; and the interfacial surface and film properties must permit the wetting or adhesion of the coating material upon the core material and must not permit the capsules to turn inside out.

Aerosols may be encapsulated by condensation of a liquid monomeric material on the core particles and initiating a rapid polymerization reaction. Aerosols may also be encapsulated by gas phase polymerization followed by condensation on the core particles, starting with a monomer vapor and initiating a rapid polymerization reaction. Component concentration, temperature, reaction time, bulk properties, etc., can be varied in the production of these encapsulated aerosols to provide a range of volatilities, stabilities, and water or water vapor permeabilities.

Aerosol encapsulation by coagulation is generally very inefficient. The coagulation approach to encapsulating with polymer films is particularly difficult. The process of coagulating polymer solution droplets with core particles and then removing the solvent does not readily produce capsules.

By using external forces the efficiency can be increased in many coagulation encapsulation systems. Liquid film capsules can be produced by coagulation, in high yields, with the aid of electrostatic forces.

#### IX Contributing Personnel

Persons who contributed to the project were Dr. Richard D. Cadle, Manager, Atmospheric Chemical Physics Department; Mr. Charles E. Lapple, Senior Scientist, as consultant; Dr. Zoila Reyes, Senior Organic Chemist;

Dr. John E. Douglas and Dr. Robert C. Robbins, Physical Chemists; and  
Mrs. Jill J. Thomas, Chemist.

A handwritten signature in cursive script, reading "Robert C. Robbins". The signature is written in dark ink and is positioned above a horizontal line.

Robert C. Robbins  
Physical Chemist

RCR:ema

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